

# ASSESSING CONDENSED AROMATIC COAL MATERIALS AS PRECURSORS FOR HIGH-VALUE CARBON PRODUCTS

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The increasing role of coal as a source of energy in the 21st century will demand environmental and cost-effective strategies for the use of carbonaceous waste products from coal combustion. Accordingly, this paper demonstrates the ability of unburned carbon from coal combustion waste to generate activated carbons by steam activation. Non-fuel uses of coal will also become more important in the coal industry of the next century. In particular, significant growth potential exists for the production of adsorbent carbons with molecular sieve properties. Anthracites can easily be tailored for this specific purpose due to their inherent fine structure.

## INTRODUCTION

The US electric power industry relies heavily on the use of coal as the primary energy source. In 1997, around 90% of the total US coal production was used in coal-fired units to generate over 55% of the total electricity<sup>1</sup>. Furthermore, coal is the most abundant fossil fuel resource in the US, and therefore it will even play an increasing role as a source of energy in the 21st century<sup>2</sup>. However, the use of coal for energy generation faces environmental challenges due to the emissions of pollutants such as NO<sub>x</sub> and SO<sub>x</sub> by coal combustion furnaces. Moreover, environmental pressures will only intensify in the next century and to guarantee a key role of coal as energy source, the conventional processes for coal utilization have to be redesigned to comply with clean air regulations. In particular, the implementation of these regulations concerning NO<sub>x</sub> emissions is being addressed in coal combustion furnaces mainly by a combination of low-NO<sub>x</sub> burners and catalytic reduction systems. Although low-NO<sub>x</sub> burner technologies efficiently decrease the emissions level by lowering the temperature of combustion, they also reduce the combustion efficiency, with a corresponding alarming rise in carbonaceous waste product from coal combustion<sup>3</sup>. In 1997, the combustion of 830 million tonnes of coal generated around 75 million tonnes of coal combustion by-products (CCBPs), mainly fly ash containing unburned carbon<sup>4</sup>. Due to the present lack of routes for their effective use, the fate of these products is mainly disposal. However, the increasingly severe regulations on disposal and the limited access to new disposal sites with the subsequent increase in the cost of disposal, will force the coal and energy industry to recycle a larger amount of CCBPs. Consequently, there is a clear need to establish environmental and cost-effective strategies for the use of these carbonaceous waste products from coal combustion.

The carbonaceous residue in fly ash, unburned carbon, is a potential precursor for the production of adsorbent carbons, since it has gone through a devolatilization process while in the combustor, and therefore, only requires to be activated. However, for new precursors to compete effectively with the conventional raw materials like wood, they must have a low cost, low mineral matter content and easily be converted into activated carbons<sup>5</sup>. The unburned carbon in the ash furnishes satisfactorily all these conditions, since it can readily be obtained from the utility industries as a by-product, it can be beneficiated

from the fly ash by commercially available techniques and it has already gone through a devolatilization process in the combustor and, therefore, only requires to be activated. However, no attempt to activate this carbonaceous waste has been conducted thus far.

In addition to the major use of coal as a fuel source, non-fuel uses like production of high-value chemicals and premium carbon products, will also become more important in the coal industry of the next century<sup>2</sup>. Significant growth potential exists for the use of coal as precursor for the production of activated carbons, due to the continuous worldwide growing demand for adsorbent materials. The main reason for this expanding market is the ubiquitous use of activated carbons as adsorbent materials in a broad range of increasing household, medical, industrial, military and scientific applications, that range from gas-phase adsorption in household air conditioning equipment and industrial emissions control, to liquid-phase adsorption for water treatment and even gold recovery. Each application is associated with a specific set of properties of the activated carbon, and precursors that can easily be converted into the required adsorbent materials will excel. This is the case of anthracites, since their fine pore structure makes them excellent raw materials for the production of adsorbent carbons with molecular sieve properties for gas separation in pollution control technologies<sup>6</sup>. However, the use of anthracites as precursors for adsorbent materials is being under-exploited, probably due to the limited number of studies assessing the possible routes for their conversion into activated carbons.

This work addresses the potential use of both unburned carbon from coal combustion and anthracites as precursors for adsorbent carbons. Both materials have highly condensed aromatic structures with a low volatile content. A single step carbonization/activation process was used for the activation of these materials, using steam as the activating agent. The porosity of the resultant activated carbons was characterized by conducting N<sub>2</sub> isotherms at 77K.

## EXPERIMENTAL PROCEDURE

**Samples** A fly ash containing unburned carbon was collected from the mechanical precipitators of unit #3 (70 MW) of the Dale power plant (Eastern Kentucky Power). The sample was screened with a 140 mesh sieve (106  $\mu\text{m}$ ), with the 140+ fraction being triboelectrostatically separated to obtain a carbon-enriched sample with a glass content of ~ 10 % volume, as determined by petrography<sup>3</sup>. A detailed description of this unburned carbon sample (UC) is given elsewhere<sup>3</sup>. The Pennsylvania anthracite (A) selected for this study contains 6.8 % ash (db) and the atomic H/C ratio is ~ 0.19. Previous studies conducted by the authors have shown that the particle size of the starting anthracite was the most critical variable that affects the properties of the resultant adsorbent carbon. Accordingly, for this study the anthracite was ground and sieved to obtain a particle size fraction 250-150  $\mu\text{m}$ .

**Activation procedure** The activation of the samples was carried out in an activation furnace, that consists of a stainless steel tube reactor and a vertical tube furnace, similar to the one used previously by the authors<sup>6</sup>. Small modifications were made in the previous design to improve the flow of steam throughout the reactor and to be able to work with a significant smaller particle size. Typically 3 - 5 g of sample was held isothermally at 850° for periods of 60 (UC-60 and A-60) and 90 (A-90) minutes while flowing steam. A reservoir was used to pump water into the reactor at low flowrates by introducing a slight head pressure of nitrogen. The flowrates used were 0.3 and 1.2 g of water/min for the unburned carbon and anthracite, respectively.

**Porosity measurements** N<sub>2</sub> adsorption isotherms at 77K were conducted in Quantachrome adsorption apparatus, Autosorb-1 Model ASIT. The BET surface areas (SA) were calculated using the adsorption points at the partial pressures 0.1

- 0.3. For the activated samples, the total pore volume,  $V_{TOT}$ , was calculated from the amount of vapor adsorbed at partial pressure 0.95.

## RESULTS AND DISCUSSION

Inherent porosity of the raw materials Figure 1 shows the  $N_2$ -77K adsorption isotherms for the raw unburned carbon (UC) and anthracite (A) and illustrates the different inherent porosity of these materials. The adsorption isotherm of the unburned carbon (UC) sample is a Type II isotherm according to the classification of Brunauer, Deming, Deming and Teller (BDDT) <sup>7</sup>. This Type II isotherm is typical for nonporous or macroporous adsorbents, on which unrestricted monolayer-multilayer adsorption can occur, and the inflexion point of the isotherm indicates completion of monolayer and the onset of multilayer coverage. Pore size distribution studies have shown that the porosity of this UC sample is mainly due to meso- and macropores, with pore widths typically over 40 nm. In contrast, the adsorption isotherm of the anthracite (A) is Type I (Figure 1), corresponding to a microporous system, as expected due to the well-known fine structure of anthracites. However, this isotherm also presents a tail as saturation pressure is approached, indicating the presence of some macropores.

Table 1 lists the BET surface areas (SA) for the precursors. The unburned carbon sample has a SA of 40 m<sup>2</sup>/g, compared to only <1 m<sup>2</sup>/g for the anthracite. The reason for the higher SA of the unburned carbon is probably due to the generation of porosity by the combustion process. The extensive and rapid devolatilization that coal undergoes in the combustor, seems to promote the generation of meso- and macropores.

Development of activated carbons from unburned carbon and anthracite All the samples were activated at 850°C for periods of 60 (UC-60 and A-60) and 90 (A-90) minutes. Table 1 lists the solid yields of the activated samples. As expected, when comparing samples with the same activation time, UC-60 and A-60, the UC presents a much higher solid yield than the anthracite, 73 % vs. 59 %, since the UC has already gone through a devolatilization process in the combustor. In fact, elemental analyses conducted in the raw UC have reported an atomic H/C ratio as low as 0.02, indicating the very low content of volatiles and the high degree of condensation of this sample. This makes the UC an attractive precursor for the production of activated carbons, since it presents much higher solid yields than conventional precursors, like wood (volatile content ~ 60%).

Figure 2 shows the  $N_2$ -77K adsorption isotherms for the steam activated unburned carbon (UC-60) and anthracites (A-60 and A-90). The three isotherms, regardless of the precursor, are Type I, with the typical concave shape to the  $P/P_0$  axis and approaching a limiting value as the saturation pressure is reached. Although the isotherm of the activated carbon produced from the unburned carbon sample, UC-60, is still Type I, the isotherm does not reach a plateau for high relative pressures. Therefore, although UC-60 has lost the meso- and macroporosity present in the precursor, it has a wider microporosity than the activated samples derived from anthracite. Pore size distribution studies and  $CO_2$  isotherms are being conducted to determine the degree of microporosity for the activated samples.

Table 1 lists the BET SA and total pore volume,  $V_{TOT}$ , of the activated carbons generated. As expected from the isotherms (Figure 2), the A-90 has the highest SA and  $V_{TOT}$ . When comparing samples activated under similar conditions but derived from different precursors, UC-60 and A-60, the activated carbon generated from the anthracite presents the highest SA and  $V_{TOT}$ . Figure 3 illustrates that these differences are not due to the precursors, but to the solid yield. Indeed, extremely good correlations were obtained between the solid yields and both the SA and the  $V_{TOT}$ , regardless of the precursor. The effect of the different flowrate of steam used to activate the unburned carbon and the anthracite is being investigated.

The activated carbons generated from the anthracite present SA significantly higher than that of previous studies conducted by one of the authors<sup>6</sup>. In fact, the SA of the sample activated after 90 minutes, A-90, presents a SA of 1037 m<sup>2</sup>/g, compared to that of 610 m<sup>2</sup>/g after six hours of activation. This is probably due to a combination of the lower flowrates (2 g of water / min vs. 12 g of water / min) and smaller particle size (250-150 µm vs. 1-3 mm) used here, resulting in more favourable conditions for the production of activated carbons.

## CONCLUSIONS

The work reported here has demonstrated for the first time the ability of unburned carbon from coal combustion waste to generate activated carbons by steam activation with a high solid yield. All the activated carbons investigated present isotherms Type I that are typical for microporous carbons, regardless of the precursor used for their production. Furthermore, the inherent porosity of the precursor does not seem to limit the surface area, neither the total pore volume of the activated carbons. However, these two properties are strongly related to the solid yields. The nature of the precursor does seem to influence the extent of microporosity, in the sense that anthracite produced activated carbons with narrower microporosity than the one derived from unburned carbon. The molecular sieve properties of the activated carbons generated from anthracites will be reported.

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Table 1. Solid yield, BET surface area and total pore volume of the raw precursors and the activated carbons generated from unburned carbon and anthracite<sup>1</sup>.

	Activation time / min	Solid yield / % weight	BET S.A. / m <sup>2</sup> /g	V <sub>total</sub> / cm <sup>3</sup> /g
UC	-	-	40	-
A	-	-	<1	-
UC-60	60	73	332	0.15
A-60	60	59	613	0.30
A-90	90	33	1037	0.47

<sup>1</sup> The solid yields and surface areas are expressed in ash free basis.

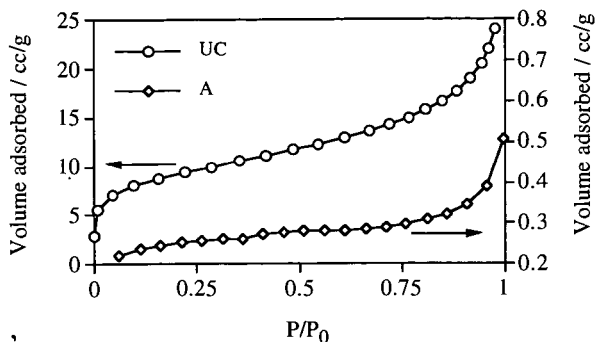


Figure 1  $N_2$ -77K adsorption isotherms for the raw unburned carbon (UC) and anthracite (A).

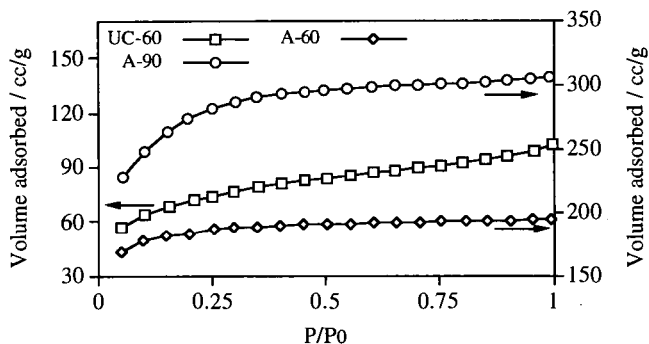


Figure 2  $N_2$ -77K adsorption isotherms for the steam activated unburned carbon (UC-60) and anthracites (A-60 and A-90).

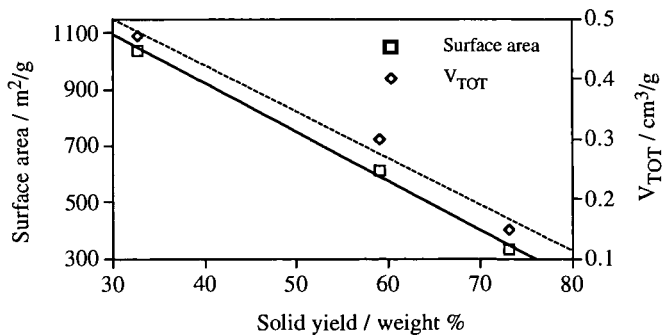


Figure 3 Relationship between solid yields, SA and  $V_{TOT}$  for all the activated carbons investigated (UC-60, A-60 and A-90).